

The University of Chicago

I. THE PEROXIDE EFFECT IN THE
ADDITION OF HALOGEN ACIDS
OF SOME ETHYLENIC
COMPOUNDS

A PART OF A DISSERTATION SUBMITTED TO
THE FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1935

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MURRAY CHURCHILL McNAB

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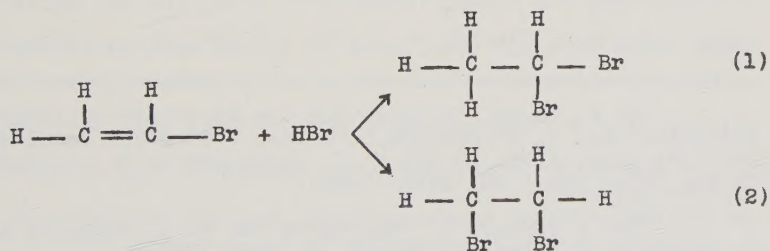
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PART I

Kharasch and Mayo¹ proved conclusively that the most important factor in the addition of hydrogen bromide to allyl bromide is the peroxide content of the latter material. Peroxide-free conditions in that case were attained either by preparing and working with materials under carefully controlled conditions or by the addition to the reaction mixture of antioxidants. It was shown that once peroxide-free conditions were attained, temperature, infra-red and possibly all other radiation, and solvents played very minor roles in directing the addition of the halogen acid except in so far as these factors influenced the peroxide effect. It became important to ascertain, therefore, to what extent other unsaturated compounds are affected by peroxides ordinarily present in these materials as impurities.

In the case of vinyl bromide it was particularly important to know whether the normal reaction proceeds according to scheme (1) or (2).



The formation of ethylene dibromide (2) is predicted by the

¹M. S. Kharasch and F. R. Mayo, J. Am. Chem. Soc., 55, 2468 (1933).

Lewis-Lucas¹ hypothesis, while the hypothesis of Kharasch and collaborators² predicts the formation of ethylidene bromide (1). Both hypotheses predict the exclusive formation of one product. A rigorous test of the merit of the two concepts is thus made possible by the study of the compounds formed under normal and under peroxide catalyzed conditions.

Previous work on the addition of hydrogen bromide to vinyl bromide is adequately summarized by Wibaut³ in a recent paper. Two papers⁴ along the same line have appeared since but they contribute little more to the theoretical explanation of the course of the reaction. Briefly, both possible addition products, 1, 1-dibromoethane and 1,2-dibromoethane, have been obtained pure and in varying proportions. The literature is distinguished by an unexplained lack of agreement in supposedly identical experiments, and much is made of the relation between the concentration of reacting substances and the addition products obtained. A more complete survey and discussion of the earlier work is not justified because the previous workers were entirely unaware of the peroxide effect which we find to be the dominating factor in the addition. Therefore, the previous investigators were seldom investigating one single factor at a time, and any agreement between their data and ours is to be looked upon as fortuitous.

¹G. N. Lewis, "Valence and the Structure of Atoms and Molecules" (A. C. S. Monograph Series). Chemical Catalogue Co., New York City, 1923, p. 89; H. J. Lucas and A. Y. Jamieson, J. Am. Chem. Soc., 46, 2475 (1924).

²For a summary of references see M. S. Kharasch and O. Reinmuth, J. Chem. Education, 8, 1703 (1931).

³J. P. Wibaut and Coworkers, Rec. trav. chim., 50, 313 (1931).

⁴G. N. Burkhardt and W. Cocker, Rec. trav. chim., 50, 837 (1931); J. P. Wibaut and J. VanDalfsen, Rec. trav. chim., 51, 636 (1932).

Factors Influencing the Addition of Hydrogen Bromide to Vinyl Bromide

The effect of peroxides.- As already mentioned, the peroxide content of the vinyl bromide is the most important single factor governing the direction and velocity of addition of hydrogen bromide to that substance. We have found that the peroxide content of a lot of vinyl bromide increases regularly from day to day after its preparation, even when the sample is kept at -78° C. in the presence of antioxidants. Since even our best antioxidants are incapable of overcoming completely the effects of comparatively large quantities of peroxides, it is obvious that the properties of the vinyl bromide in any addition experiment will depend upon a constantly varying factor, and it is not surprising that exact duplication of results has been attained only with great difficulty.

It has been found that 1,1-dibromoethane is the product of the "normal" addition taking place under peroxide-free conditions. On the other hand, it has been demonstrated that the addition of hydrogen bromide to vinyl bromide leads to a rapid formation of 1,2-dibromoethane if no special precautions are taken to remove peroxides. Furthermore, temperature, light and solvent (except acetic acid) have no effect on the direction, although they presumably modify the velocity of this peroxide-catalyzed addition. The same result is obtained whether the addition is carried out in air or whether air is excluded. This was not the case with allyl bromide and therefore these results indicate an apparently greater sensitivity of vinyl bromide than of allyl bromide to traces of peroxides. Thus, while a very low concentration of peroxides in allyl bromide would cause only a minor variation from the normal addition, a similar concentration in vinyl bromide causes the occurrence of the peroxide-catalyzed reaction

to the exclusion of the normal addition. However, because the normal addition to vinyl bromide is only about one-tenth as fast as to allyl bromide, the same concentration of peroxide may exert a proportionally greater effect on vinyl bromide by virtue of the slowness of the competing normal reaction. Hence, while we may not say rigorously that vinyl bromide is more susceptible to the oxygen effect than allyl bromide, the effect obviously shows up to a greater extent.

The sensitivity of vinyl bromide to the peroxide effect is such that none of the normal addition product is obtained under any circumstances except in the presence of antioxidants or acetic acid or ferric chloride. However, the amount of 1,1-dibromoethane formed in acetic acid solution never exceeds 20 per cent in the absence of antioxidants. Such an effect of acetic acid for this exceedingly peroxide-sensitive system could have been anticipated from the much more pronounced effect of this solvent in the case of the less peroxide-sensitive allyl bromide.

The effect of antioxidants.- The following table shows the effect of various antioxidants on the addition of hydrogen bromide to vinyl bromide in the absence of solvents and air. It is shown that antioxidants are unable to overcome completely the effect of peroxides in many cases and the amount of normal product obtained depends on both the concentration of peroxides and the nature of the antioxidants used. However, with vinyl bromide of very low peroxide content and in the presence of good antioxidants, the product is always 1,1-dibromoethane. Diphenylamine, thiophenol and thiocresol are shown to be satisfactory antioxidants, the first being the least effective of the three. Phenyl-naphthylamine, dimethylaniline, hydroquinone and isocyanides are found to be less effective and ammonium bromide and diphenyl ether, as

TABLE I

THE ADDITION OF HYDROGEN BROMIDE TO VINYL BROMIDE IN THE ABSENCE OF SOLVENTS AND AIR AND THE PRESENCE OF ANTIOXIDANTS

No.	Antioxidant	Mole	Temp.	Reaction Time	% ^b Yield	% ^b 1,1	Peroxide Test ^c	Re- marks
A. At Room Temperature								
33 ^d	Diphenylamine	0.02	Room	3 days	5	...		
38	Diphenylamine	.01	Room	16 days	35	100		
68	Diphenylamine	.02	Room	68 days	79	100		
95 ^a	Phenyl- β -naphthyl-amine	.024	Room	48 days	84	78	1	
146	Dimethylaniline	.013	Room	10 days	50	96	0	
53	Ammonium bromide	.036	Room	4 days	98	2		
125 ^a	Propionitrile	.097	Room	3 days	94	5	2	
147	Propionitrile + dimethylaniline	.097 .013	Room	2.5 days	35	100	0	
148	Propionitrile + phenyl- β -naphthylamine	.097 .016	Room	2.5 days	34	100	0	
149	Propionitrile + thiocresol	0.097 .028	Room	2.5 days	32	100	0	
92	Benzonitrile	.054	Room	2.5 days	88	25	0	
93	Phenylacetronitrile	.046	Room	2.5 days	82	28	0	
120 ^a	<i>T</i> -Butyl isocyanide	.069	Room	2.5 days	90	100	0	
136 ^a	<i>T</i> -Butyl isocyanide	.069	Room	4 days	92	63	2	
113 ^a	<i>T</i> -Butyl isocyanide	.047	Room	4 days	97	2	4	
124	<i>T</i> -Butyl isocyanide + diphenylamine	.047 .021	Room	2.5 days	82	100	1	
58	Butyl mercaptan	.045	Room	18 days	10	...		
55	Thiophenol	.032	Room	29 days	10	...		
66	Thiophenol + manganese chloride	.032 .0002	Room	70 days	70	100		
52	Hydroquinone	.032	Room	3 days	20	...	) Large quantity of tar obtained	
89	Hydroquinone	.032	Room	53 days	50	30		

TABLE I (Continued)

No.	Antioxidant	Mole	Temp.	Reaction Time	% ^b Yield	% ^b 1,1	Peroxide Test ^c	Re-marks
56	Diphenyl ether	.021	Room	1 day	96	0		
128	Nitric oxide (tube filled with gas)		Room	3 days	45	100		Large quantity of polymerized products

B. At Higher Temperatures

43	Diphenylamine	.021	100	1 day	82	32		
47 ^a	Diphenylamine	.021	76	2 days	92	1		
51	Diphenylamine	.042	76	2 days	93	24		
85	Phenyl- β -naphthylamine	.024	76	2 days	86	0		
86	Thiophenol	.032	76	2 days	80	17		
105 ^a	Diphenylamine	.021	56	4 days	81	17	1	
99	Thiophenol + manganese chloride	.032 .0002	56	2 days	48	78	0	
109	Thiophenol + manganese chloride	.0002	56	4 days	72	78	0	
122	Diphenylamine	.021	46	5 days	92	7	4	
134	Phenyl- β -naphthylamine	.024	46	5 days	92	4	1	
121 ^a)	Thiophenol +	.04	46	5 days	86	77	0	
143)	manganese chloride	.0002			90	32	3	

C. Runs made 8 cm. from 500 W lamp

49	Diphenylamine	.021	Room	16 hrs.	90	0		
77	Phenyl- β -naphthylamine	.024	Room	16 hrs.	92	0		
78	Thiophenol + manganese chloride	.032 .0002	Room	16 hrs.	84	0		
101	Diphenylamine	.021	5	16 hrs.	78	12	0	
137	Thiophenol + manganese chloride	.032 .0002	5	16 hrs.	49	83	0	

TABLE I (Continued)

No.	Antioxidant	Mole	Temp.	Reaction Time	% ^b Yield	% ^b 1,1	Peroxide Test ^c	Re-marks
140	Thiocresol+manganese chloride	.028 .0002	5°	16 hrs.	64	79	0	

^aOne to several duplicate runs giving essentially the same results are omitted.

^bYields as given represent the fraction of the theoretical yields of dibromoethanes recovered after washing, drying, and distillation. Because of unavoidable and comparatively large losses in working with small quantities of material, many runs in which theoretical yields were undoubtedly obtained are credited with yields of 70-98 per cent.

The column headed "%1,1-" gives the percentage of 1,1-dibromoethane in the pure addition product, the remainder being 1,2-dibromoethane.

^cJust before starting many runs, a few drops of the stock vinyl bromide were tested qualitatively for peroxides with a few crystals of ferrous ammonium sulfate and about 1 cc. of 10 per cent ammonium thiocyanate solution. "0" indicates no immediate color change and the absence of peroxides within the sensitivity of the test. "4" indicates the presence of comparatively large quantities of peroxides as shown by the immediate development of a strong red coloration. "1," "2," and "3" indicate intermediate stages.

^d1.51 moles of hydrogen bromide was used in the first experiment listed, and 1.58 moles in all of the others.

anticipated, are without effect. We are satisfied that the weak effect exerted by some nitriles is due to the presence of isomeric isocyanides in the materials.

The relationship between the effectiveness of the antioxidants and the peroxide content of the vinyl bromide is brought out in a most striking manner with tertiary butyl isocyanide. When a sample of vinyl bromide freshly distilled, contains only the merest trace of peroxides, and is treated with hydrogen bromide in the presence of this antioxidant, the product is invariably pure 1,1-dibromoethane. The same lot of vinyl bromide, upon standing for one or two days, definitely shows an increase in peroxide content, and the proportion of the "normal" product

formed upon the addition of hydrogen bromide under the same conditions may vary from 50 to 90 per cent. After three or four days' standing, the vinyl bromide gives a fairly strong peroxide test and adds hydrogen bromide to give practically quantitative yields of 1,2-dibromoethane. This isocyanide is thus only a sufficiently powerful antioxidant to exert an effect when the peroxide content of the vinyl bromide is extremely low. The validity of this statement has been substantiated by thirty experimental runs in which the peroxide content varied in the manner indicated above and absolutely concordant results were obtained.

There is no evidence that any antioxidant has any retarding effect on the normal addition if we assume that the velocity of the normal addition is that found in the presence of diphenylamine and mercaptans. However, it should be noted that an isocyanide, nitriles (including hydrogen cyanide from potassium cyanide) and nitrobenzene cause a tremendous acceleration of the normal addition even when various antioxidants are also added to counteract the peroxide effect. The usual interpretation of such results on the basis of the dielectric constant of the medium is, in our estimation, inadequate. There seems also to be some variation in velocity with different antioxidants in the absence of solvents. In the presence of substances which we term antioxidants, we have obtained both very rapid and very slow addition to give 1,1-dibromoethane, and we have also experienced the formation of 1,2-dibromoethane in the presence of the weaker antioxidants and comparatively large amounts of peroxides. Our conclusion is that antioxidants have no effect on the direction of addition of hydrogen bromide except that they tend to overcome the peroxide effect.

The effect of temperature.- In the case of other ethylene compounds studied, increased temperature exaggerates the peroxide effect, and with a system as sensitive to peroxides as vinyl bromide, the increased peroxide effect might easily become the dominating factor in the reaction, even in the presence of anti-oxidants. The initial peroxide content of the system would thereby produce an effect far greater than under lower temperature conditions and the ability to duplicate experiments would resolve itself into our ability to prepare lots of vinyl bromide of the same peroxide content.

We attribute the formation of the 1,2-isomer at 100° C. and 76° C. (Table I) in the presence of antioxidants to the effect of the peroxides as exaggerated by temperature rather than as a temperature effect (per se). Thus when the vinyl bromide contains only a minute trace of peroxide, thiophenol is capable of overcoming its effect and the product is about 70-80 per cent of 1,1-dibromoethane at 56° C. On the other hand, diphenylamine, a weaker antioxidant, is unable to overcome the peroxide effect as exaggerated at this temperature and also at 46° C. However, even thiophenol is unable to overcome the effect of an increase in the peroxide content of the vinyl bromide, at this temperature, and the addition product contains only 32 per cent of 1,1-dibromoethane.

The effect of light.- The last results in Table I show that at room temperature under strong illumination, the addition product is 1,2-dibromoethane, even in the presence of good anti-oxidants. Under similar conditions at 5° C., up to 80 per cent of the normal product is formed. Since it was shown in the previous section as well as in the paper on allyl bromide that temperature lowering greatly decreases the peroxide effect, the experiments mentioned above indicate that light has no effect on

the direction of addition of hydrogen bromide to vinyl bromide except that it increases the magnitude of the peroxide effect. Note also that strong illumination increases tremendously the velocity of both the "normal" and "peroxide-catalyzed" additions.

The effect of solvents.- Although fewer solvents (Table II) were used by us than in the case of allyl bromide, the results are as unmistakable as in that case, that the effect of the solvent on the order of addition is negligible, except as it may influence the peroxide effect. The effect of various materials in accelerating the rate of the reaction is without doubt related to the dielectric constant of the solvent but in no case does that effect outweigh that of the peroxides. The difficulties in duplicating runs are directly connected with the day-to-day variation in the peroxide content of the vinyl bromide. On the whole, it can be readily noted that in glacial acetic acid the yield of the 1,1-dibromoethane seldom exceeds 20-25 per cent in the absence of an antioxidant. This result is in accord with the great susceptibility of vinyl bromide to traces of peroxides and the fact that glacial acetic acid is a poor antioxidant. In the presence, however, of better antioxidants, the yield of the normal product is increased and may vary between 65 and 100 per cent, depending upon the antioxidant and the age of the vinyl bromide, as shown in Table II. Other solvents, such as acetic acid containing 5 per cent water, acetyl bromide, and nitrobenzene show the same trend, and fair yields of the 1,1-isomer may be obtained by the use of good antioxidants.

The effect of metal and surface catalysts.- As previously stated the effect of antioxidants is to eliminate the peroxide effect. This, of course, may be accomplished in a variety of ways, and hence the variety of reagents that may be employed is large.

TABLE II

THE ADDITION OF HYDROGEN BROMIDE TO VINYL BROMIDE IN THE
PRESENCE OF SOLVENTS AND ANTIOXIDANTS^a

No.	Solvent	Antioxidant	Mole	Reaction Time	Yield %	% ^b 1,1-	Remarks
44	Glacial acetic acid	Diphenylamine	0.01	10 days	40	100	
71		Diphenylamine	.021	66 days	85	70	
62		Phenyl- β -naph- thylamine	.018	26 days	70	63	
67		Thiophenol +	.032	32 days	48	100	
72		manganese chloride	.0002	63 days	70	86	
63		Thiophenol	.032	26 days	80	84	
152		Thiocresol	.028	11 days	48	96	HBr only, not vinyl bromide, dried and distilled (in vacuo)
40		Diphenylamine	.01	16 hrs.	79	13	Run 8 cm. from watt lamp
79	Glacial acetic acid	Phenyl- β -naph- thylamine	.032	16 hrs.	90	28	
80	Acetic acid	Thiophenol +	.064	16 hrs.	90	20	
		manganese chloride	.0002				
84		Phenyl- β -naph- thylamine	.016	56 days	92	61	
83	(Mixture of acid & water used, contain- ing 5% by weight of water)	Thiophenol	.032	55 days	73	85	
		Thiocresol	.028	11 days	80	89	HBr only, not vinyl bromide, dried and distilled (in vacuo)
65	Acetyl-bromide	Phenyl- β -naph- thylamine	.016	69 days	92	92	
74	Acetyl-bromide	Thiophenol	.033	63 days	90	63	Peroxide test 2
73	Acetyl-bromide	Thiophenol +	.033	64 days	64	69	Peroxide test 2
		manganese chloride	.0002				

TABLE II (Continued)

No.	Solvent	Antioxidant	Mole	Reaction	Yield	% ^b	Remarks
				Time	%	1,1-	
114	Nitrobenzene	Diphenylamine	.032	2 days	38	50	Peroxide test 0
119	Nitrobenzene	γ -butyl isocyanide	.069	5 days	71	96	
88	Nitrobenzene	Thiophenol	.065	4 days	34	54	
117	Nitrobenzene	Thiophenol + manganese chloride	.065 .0002	20 days	62	70	

^aExcept as otherwise noted, the runs in this table were made at room temperature in the dark, and in the absence of air. 2.0 moles of hydrogen bromide was used in all of these experiments except in No. 152 where 4.0 moles was used. 1.5 moles of solvent was used in all cases except that in the last four experiments listed, 1.0 mole of nitrobenzene was used.

^bSee footnote b under Table I (p. 7).

Ferric chloride acts as antioxidant, but it also accelerates tremendously the rate of formation of the normal product, 1,1-dibromoethane. Furthermore, light apparently has no effect upon the order of addition in the presence of the iron salt. These facts may be accounted for also on the basis that the iron-catalyzed addition is fast enough to obscure even the peroxide-catalyzed addition (Table III).

Of the other metallic salts used, mercuric bromide,¹ manganese chloride,² and potassium cyanide, none appears to have any effect on the addition in the liquid phase. Note, for instance, that when a sample of vinyl bromide of moderate peroxide

¹J. P. Wibaut, *op. cit.*, claims that this material acts as a catalyst for the vapor-phase addition.

²Manganese salts have been found to catalyze the oxidation of sulfur compounds. Since manganese chloride was used in conjunction with some of the antioxidants, its effect by itself was also tested.

content is treated with hydrogen bromide in the presence of hydrogen cyanide, none of the 1,1-dibromoethane is formed. However, under the same conditions in the presence of diphenylamine, 48 per cent of this product is readily obtained. Anhydrous aluminum chloride caused so much polymerization of the vinyl bromide that no addition product was isolated.

TABLE III

THE ADDITION OF HYDROGEN BROMIDE TO VINYL BROMIDE IN THE PRESENCE OF METALLIC SALTS AND SURFACE CATALYSTS^a

No.	Catalyst	Mole Catalyst	Reaction Time	Yield % ^b	% ^b 1,1-	Per-oxide Test ^c	Remarks
48	Anhydrous AlCl ₃	0.019	1 day	0	0		Only tar obtained.
39	Anhydrous FeCl ₃	.022	1 day	88	100		
41	Anhydrous FeCl ₃	.022	6 hrs.	38	100		Run 8 cm. from 500 watt lamp.
50	Anhydrous FeCl ₃	.022	2 hrs.	72	100		Tar formation accounts for low yield in 41.
144	Mercuric bromide	.04	3 days	95	0	1	
59	Manganese chloride	.0002	1 day	97	0		
64	Manganese chloride	.0002	26 days	90	24		1.5 moles of glacial HAC used as solvent.
145	Potassium cyanide	.023	3 days	96	0	1	
156	Potassium cyanide	.023	4 days	88	48	1	0.01 mole diphenylamine added.
155	Asbestos ^d		3 days	92	0	0	
156	Glass wool ^d		3 days	91	0	0	

^aExcept as otherwise noted, the runs in this table were made at room temperature, in the dark, and in the absence of air. 1.58 moles of hydrogen bromide was used in all runs except No. 64, where 2.0 moles was used.

^{b,c}See notes b and c under Table I (p. 7).

^d2-3 cm. of the bomb tubes was filled loosely with these materials. The asbestos commercially acid-washed and ignited material, was further washed with acid to remove remaining traces of iron salts. Cf. Kharasch and Mayo, op. cit.

As was to be expected, pure asbestos and glass wool have no apparent effect on the order of addition, and the results of the addition do not differ in any way from those obtained in their absence with samples of vinyl bromide of the same peroxide content.

Experimental Part

Preparation of vinyl bromide.- Vinyl bromide was prepared by dropping ethylene bromide (purified by freezing) into an excess of 20 per cent solution of potassium hydroxide in 95 per cent ethyl alcohol. The vapors were passed upward through a reflux condenser kept at 20°. The crude product was condensed directly at -80°, washed at 0° with water, dried over calcium chloride, and distilled. About 0.5 per cent of diphenylamine was then added and the mixture was kept at -80°. This diphenylamine had little effect on decreasing the formation of peroxides (for possible explanation consult Kharasch and Mayo, op. cit.). Yield = 60 per cent theory.

Technique of additions.- The apparatus used in this work was the same as is described by Kharasch and Mayo.¹ In most cases the amount of vinyl bromide used was 6 g. The quantities of other materials used are given in the tables on the basis that the quantity of vinyl bromide used was 1 mol. Solvents, antioxidants, and catalysts were usually put into the receiver bomb tube and the hydrogen bromide and vinyl bromide were distilled into them. The unreacted vinyl bromide and solvents not removed by washing were easily removed from the addition product by fractional distillation. The calculation of the yields is described in note b of Table I. The composition of the addition product was determined from the index of refraction of the mixture of purified dibromo-

¹Op. cit.

ethanes and was always checked qualitatively by the boiling range. The indices of refraction of the two dibromoethanes were determined to be $n_{20}^{d_{1,1-}}$, 1.5123; 1,2 1.5380. Wibaut¹ has shown that the index of refraction of these two compounds is a straight line function of the composition.

Summary and Conclusions

1. It has been shown that under well-defined conditions, hydrogen bromide can be added to vinyl bromide to give either 100 per cent of ethylidene bromide or 100 per cent of ethylene dibromide.

2. It has been demonstrated that the formation of ethylidene bromide is the "normal" addition.

3. It has been demonstrated that peroxides in the vinyl bromides are responsible for the formation of 1,2-dibromoethane.

4. The effects of solvents, temperature, light, antioxidants, and different surfaces and salts upon the velocity and direction of addition have been studied. The general conclusion has been reached that the peroxides are probably the most important single factor governing the direction of addition and that all other agents exert their specific effects not upon the organic unsaturated molecule itself, as assumed in the literature, but either upon the peroxide molecules or in activating oxygen liberated by the decomposition of peroxides.

¹Op. cit.

THE ADDITION OF HYDROGEN BROMIDE TO PROPYLENE

The addition of halogen acids to propylene has been studied by a number of investigators¹ under a variety of experimental conditions. The effects of the following factors on the ease of addition were evaluated: temperature,^{1^{a,e,f,h,i}} concentration of halogen acid in the anhydrous addition mixture,^{1^f} pressure,^{1^{f,k}} concentration of water,^{1^f} catalysis by metals,^{1^f} metallic salts in solvents,^{1^{j,l}} metallic salts and surfaces in the vapor phase,^{1^{i,l}} excess halogen acid,^{1^f} and air.^{1^l} In spite of all these variations, the final product of all the reactions was always the isopropyl halide. While Michael^{1^d} isolated a very small amount of normal propyl iodide from the reaction between aqueous hydriodic acid and gaseous propylene at 0° C., his method of analysis of the addition product was far too inexact to justify the great significance that has been attached to his observation. The formation of a hexyl halide as by-product was studied by Maass and collaborators.^{1^{e,f,g}}

¹(a) M. Berthelot, *Ann.*, 104, 184 (1857); (b) E. Erlenmeyer, *ibid.*, 139, 228 (1866); (c) A. Butlerow, *ibid.*, 145, 275 (1868); (d) A. Michael, *J. Prakt. Chem.*, (2) 60, 445 (1899); (e) O. Maass and C. H. Wright, *J.A.C.S.*, 46, 2664 (1924); (f) O. Maass and C. Sievertz, *ibid.*, 47, 2883 (1925); (g) H. Sutherland and O. Maass, *Trans. Roy. Soc. Can.*, 20, 499 (1926); (h) H.S. Sutherland and O. Maass, *Can. J. Research*, 5, 48 (1931); (i) J.P. Wibaut, J.J. Diekmann, and A.J. Rutgers, *Proc. Acad. Sci. Amsterdam*, 27, 671 (1924); *Rec. trav. chim.*, 47, 477 (1928); (j) J.P. Wibaut, *Z. Elektrochem.*, 35, 602 (1929); (k) United States Patent 1,518, 182, Curme, Carbide and Carbon Chemical Corporation, Chem. Zenir., 1, 1129 (1925); (l) Canadian Patent 258, 816, English Patent 235, 547, French Patent 599,595. Weber Schrader, and Wiedbrauch, Goldschmidt, *A. G.*, *ibid.*, 1, 179 (1927).

Our interest in the addition of hydrogen bromide¹ to propylene was aroused by our observations that the direction of addition of hydrogen bromide to allyl bromide,² allyl chloride,³ vinyl bromide,⁴ and butene-1⁵ is determined by the peroxide content of the reaction mixture. It has been shown also that the peroxide effect can be overcome by the use of good antioxidants. An investigation was therefore undertaken to determine whether isopropyl bromide is the normal or the peroxide-catalized addition product.

Table IV is a summary of our results. Briefly, the addition of hydrogen bromide to propylene, in the presence or absence of air and the presence or absence of any of a wide selection of (for this type of reaction) excellent antioxidants always resulted in practically quantitative yields of isopropyl bromide. On the other hand, the presence of benzoyl peroxide or ascaridole modified profoundly the course of the addition and the product of the reaction was largely, if not all, normal propyl bromide.

TABLE IV
THE ADDITION OF HYDROGEN BROMIDE TO PROPYLENE^a

No.	Moles HBr ^b	Antioxidant or Peroxide	Moles	Air ^c	Temp. °C.	Reac- tion Time	Yield % ^d	% iso-	Re- mark
1	1.23	Diphenylamine	0.024	Absent	Room	3 hrs.	70	100	
2	1.23	Diphenylamine	.024	Absent	Room	18 hrs.	95	100	

¹An investigation of the addition of other halogen acids to substituted ethylenes is now under way in this laboratory.

²M. S. Kharasch and F. R. Mayo, J. Am. Chem. Soc., 55, 2468 (1933).

³M. S. Kharasch and R. S. Shane, unpublished work.

⁴M. S. Kharasch, M.C. McNab and F.R. Mayo, J.A.C.S., 55, 2521 (1933).

⁵M. S. Kharasch, R. S. Shane and W. M. Ryan, unpublished work.

TABLE IV (Continued)

No.	Moles HBr ^b	Antioxidant or Peroxide	Moles	Air ^c	Temp. °C.	Reac- tion Time	Yield % ^d	% iso.	Re- marks
3	1.23	Tertiary butyl isocyanide	.028	Absent	Room	18 hrs.	95	100	
4	1.23	Tertiary butyl isocyanide	.070	Absent	Room	18 hrs.	95	100	
5	1.23	Thiocresol + MnCl ₂	.032 .0001	Absent	Room	18 hrs.	95	100	
6	1.23	Thiocresol + MnCl ₂	.048 .0001	Absent	Room	18 hrs.	95	100	
7	1.23	Thiocresol + MnCl ₂	.08	Absent	Room	18 hrs.	95	100	0.15 mole propyl- onitrile also present
8	1.23	Thiocresol + MnCl ₂	.08 .0001	Absent	0	18 hrs.	95	100	
9	1.23	None		Absent	Room	18 hrs.	95	100	
10	1.23	Thiocresol + MnCl ₂	.16 .0001	Absent	Room	18 hrs.	95	100	
11	1.23	Benzoyl peroxide	.041	Absent	Room	18 hrs.	90	13	
12	1.23	Benzoyl peroxide	.062	Absent	-78	40 hrs.	90	70	
13	1.23	(Oxygen)		Present	Room	18 hrs.	95	79	Oxygen passed through liquid propylene at -78° for ten minutes before solution of hydro- gen bromide in propylene.
31	1.25	Benzoyl peroxide	.074	Present	Room	17 hrs.	25	13	HBr passed in very slowly
32	1.30	Ascaridole	.11	Present	Room	17 hrs.	17	2	
33	0.96	Benzoyl peroxide	.074	Present	-78	15 mins.	41	4	HBr passed in rapidly
34	1.23	Ascaridole	.13	Present	-78	32 mins.	48	0	

^aThe propylene used was obtained in compressed form from a commercial source. Hydrogen bromide was prepared from tetralin and bromine as described by Kharasch and Mayo, op. cit. Tertiary butyl isocyanide was the Kahlbaum product. The other organic materials were obtained from the Eastman Kodak Co. and were used without purification.

^bFor runs Nos. 1-13, 4.2 g., for Nos. 31-34, 3.5 g., of propylene was used. The quantities of hydrogen bromide, antioxidants, and peroxides are calculated on the basis that one mole of propylene was used.

^cIn those runs in which air was absent, the propylene was condensed in a bomb tube with the antioxidant or peroxide. Hydrogen bromide was then condensed in a second bomb tube at the temperature of boiling nitrogen. The hydrogen bromide was then distilled (in vacuo) into the first bomb tube according to the technique of Kharasch and Mayo, op. cit. In those runs in which air was present, hydrogen bromide was dissolved at -78° in liquid propylene to which the peroxide (if any) had already been added. The bomb tube was then sealed off without taking any precautions to exclude air or moisture.

^dThe yields as given in this column represent the final weights of propyl bromides recovered. In runs 31-32, an attempt was made to remove the peroxides by washing with concentrated sulfuric acid. Difficulties in separation of layers and formation of emulsions caused large losses of addition product. In Nos. 33-34 the peroxides did not dissolve in the cold reaction mixture to any considerable extent, and the mixture was therefore poured off the undissolved peroxides at low temperatures. Considerable quantities of addition product were lost with the rejected mass of peroxides. These circumstances explain the low apparent yields in the runs. The actual degree of completeness of these four reactions was probably of the order of 80 per cent or more.

^eThe composition of the purified addition product was determined by its index of refraction. We assumed the index of refraction of the mixture to be a linear function of its composition. In the column designated "% iso-" is given the fraction of iso-propyl bromide in the purified addition product. The remainder of the addition product was normal propyl bromide. The boiling ranges of the addition products were consistent with their compositions as calculated by their indices of refraction.

Since publication of the foregoing table, Sherrill, Mayer, and Walter,¹ on the basis of a study of the addition of hydrogen bromide to pentene-1 and heptene-1 in glacial acetic acid, hexane and water, conclude that the solvent is the dominant factor governing the direction of addition, and that the peroxide effect is

¹M. I. Sherrill, K. E. Mayer, and G. F. Walter, J.A.C.S., 56, 926 (1934).

insignificant or non-existent. They reject the work on propylene on the ground that the small quantities of materials employed furnish yields which are "not very significant."

Accordingly, further repetition of the study of the addition of hydrogen bromide to propylene was carried out using larger quantities of reagents. Identification of the products was made by boiling points, refractive indices and the preparation of mercury derivatives. Using 1.4 mol (85 g.) of hydrogen bromide, one mol (31.5 g.) of propylene and two grams of ascaridole as peroxide we obtained, working at -80° , both without a solvent and using glacial acetic acid, an 80 per cent yield of 100 per cent n-propyl bromide, b. p. $70-71^{\circ}$, n 1.4340 and with a mercury derivative melting at 137.2° . With carbon tetrachloride as a solvent an 18 per cent yield was obtained. Similar experiments using two grams of diphenylamine as antioxidant gave, with no solvent, or glacial acetic acid or carbon tetrachloride, respectively, 61.65 and 44 per cent yields of 100 per cent isopropyl bromide, b. p. $59-60^{\circ}$ n 1.4250 ($\pm$ 0.0001) and a mercury derivative melting at 92.6° . These results are in accord with Table IV in every detail.

These facts indicate either that the rate of the normal reaction of propylene with hydrogen bromide is sufficiently rapid to overcome the effect of minute traces of peroxides, or that propylene does not form peroxides very readily in air. This latter hypothesis finds some substantiation in the run in which oxygen was first bubbled through the propylene at -78° for ten minutes. The addition product in this experiment consisted of 21 per cent normal propyl bromide. It is possible, therefore, that the failure of earlier investigators to obtain the normal halide is to be attributed to the fact that propylene is a gas and that

under the experimental conditions of work with it, the gas displaces most of the oxygen from the system before sufficient quantities of peroxides can be formed. It is possible, also, that there may be little tendency toward peroxide formation in the gaseous phase.

It is of interest to note that lowering the temperature has the same apparent result in decreasing the peroxide effect as it has in the case of the other substituted ethylene compounds. The yield of the peroxide catalyzed product, i.e., normal propyl bromide, is only 30 per cent at -78° and 87 per cent at room temperature in the absence of air.

A more thorough investigation to include the effects of solvents, temperature and light was not undertaken because we have previously demonstrated that these factors have no effect by themselves, but only an indirect effect through their action on peroxides. Therefore, probably little more could be learned than what we have already discussed in our previous publications.

Summary

1. The addition of hydrogen bromide to propylene in air and in the presence of antioxidants leads to the formation of pure isopropyl bromide.

2. In the presence of added peroxides, e.g., benzoyl peroxide or ascaridole, hydrogen bromide may add to propylene to give practically quantitative yields of normal propyl bromide.

THE ADDITION OF HYDROGEN BROMIDE TO ALLYL ACETIC ACID

Linstead and Rydon¹ extended observations, on the directive effect of peroxides in the addition of hydrogen bromide to unsaturated compounds, to allyl acetic acid. These investigators showed that the normal product of the reaction is the γ -bromo valeric acid, while in the presence of benzoyl peroxide the δ -bromo valeric acid is obtained in excellent yields. However, they claim that in solvents such as hexane the peroxide effect is negligible or of "secondary importance." This conclusion is based on the observation that the addition of hydrogen bromide to allyl acetic acid in hexane as the solvent invariably gave δ -bromo valeric acid in the presence or absence of antioxidants.

The addition of hydrogen bromide to allyl acetic acid with and without solvents has now been repeated in this laboratory using the technique described by Kharasch and Mayo.² The table below is a summary of some results on the addition of hydrogen bromide to allyl acetic acid with hexane as the solvent.

Time	Allyl Acetic Acid in Hexane	Antioxidant or Peroxide in mols.	Yield %	M.P. °C.	Produce
12 days	10 gms. (.1 mol)	.0024 mols diphenylamine	90 $\pm$ 10	22	γ -bromvaleric acid
12 days	10 gms. (.1 mol)	.0024 mols thiocresol	90 $\pm$ 10	22	γ -bromovaleric acid
10 days	10 gms. (.1 mol)	.0006 mols ascaridole	90 $\pm$ 10	40	δ -bromvaleric acid

¹R. P. Linstead and H. N. Rydon, Nature, 132, 643 (1933).

²M. S. Kharasch and F. R. Mayo, J. A. C. S., 55, 2468 (1933).

The amount of solvent used was the same as in the experiments of Boorman, Linstead and Rydon¹ and the products of the reaction were identified in accordance with their direction. The γ -bromo valeric acid was further confirmed by the preparation of the γ -hydroxy valeramide.² It is evident that these data are in complete agreement with our previous statements that peroxides and not solvents control the direction of addition. Incidentally, one more example cited against us by Sherrill, Mayer and Walter³ has thus been shown to be due to lack of an exact control of experimental conditions.

Experimental Part

Preparation of allyl acetic acid.- Allyl bromide was prepared by the method of Gilman.⁴ Ethyl Allylmalonate was then prepared from pure allyl bromide and purified malonic ester according to the method given by Gilman⁵ for the preparation of ethyl n-butylmalonate. The allylmalonic ester was purified by distillation in vacuo and converted to allyl acetic acid by the method of Gilman⁶ omitting the final steam distillation. The allyl acetic acid was first separated from the aqueous solution and the aqueous layer extracted with ether. The allyl acetic acid was then dried by distilling with twice its volume of benzene and was further purified by fractional distillation in vacuo. Yield 60 per cent theory, b.p. 93° C. 6 mm., M.P. 22.5° C.

¹E. J. Boorman, R. P. Linstead and H. N. Rydon, J. C. S., 578 (1933).

²Ibid.

³M. L. Sherrill, K. E. Mayer and G. F. Walter, J. A. C. S., 56, 926 (1934).

⁴Gilman, Org. Synth. Coll. Vol., p. 24.

⁵Ibid., p. 245.

⁶Gilman, Org. Synth., Vol. XI, 76.

